

# PATENT SPECIFICATION

(11) 1 480 112

1 480 112

- (21) Application No. 40640/74 (22) Filed 18 Sept. 1974  
 (31) Convention Application No. 2347755 (32) Filed 22 Sept. 1973 in  
 (33) Federal Republic of Germany (DT)  
 (44) Complete Specification published 20 July 1977  
 (51) INT CL<sup>2</sup> C08F 236/06 2/26 6/22 (C08F 236/06 220/04 220/42  
 236/08)  
 (52) Index at acceptance  
 C3P 102 2D1A2 2D1B2 2K2 2K7 2K8 7D2A1 7K2 7K8  
 8D1A 8D1B 8D3A 8D3B 8D4 8K2 8K7 8K8 D11  
 P1C P1E2 P1F P2A4 P2C P4A P6A P6G T1A T1C  
 (72) Inventors ERNST SCHWINUM, HEINZ HORNIG and  
 MARTIN MATNER



## (54) PRODUCTION OF SHAPED ARTICLES

(71) We, BAYER AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 509 Leverkusen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the production of shaped articles.

A process frequently used for the production of shaped articles, especially hollow bodies, from natural rubber latices and from synthetic rubber latices, i.e. dispersions of film-forming synthetic polymers, involves dipping a mould made of wood, glass, porcelain, metal or plastics material first into a solution containing a material which coagulates rubber latex and then into a natural rubber or synthetic rubber latex. A film of rubber is formed on the surface of the mould as the rubber is precipitated from the latex by the coagulant material adhering to the mould. The articles produced by this process are referred to hereinafter as "dipped articles", and the process is referred to as the "Koagulant" process.

The thickness and surface quality of the rubber film are dependent to a large extent on the type of coagulant material and of rubber latex used. The latices which may be used in this process are latices of natural rubber or of synthetic polymers, preferably polychloroprene, polyisoprene and butadiene-acrylonitrile copolymers. Dipped articles made from butadiene - acrylonitrile copolymers are generally more resistant to oils, fats and organic solvents than dipped articles made from polychloroprene or natural rubber. For this reason, rubber gloves in particular are produced with advantage from butadiene - acrylonitrile copolymer latices.

The butadiene - acrylonitrile copolymer latices used to date have insufficient coagulation properties since it takes a long time to

obtain films having sufficient thickness and the films obtained have a rough surface. In addition, the films have inadequate strength, the wet gel strength of unvulcanized films being far from satisfactory and the tensile strength and tear resistance of vulcanized films being limited and thus restricting the serviceability of the dipped articles.

It has now been found that dipped articles having a high tensile strength and tear resistance can be obtained from latices which are made from the monomers specified herein-after by polymerisation in aqueous emulsions using radical formers as catalysts and alkylaryl sulphonates as emulsifiers at specific concentrations and pH-values which also have a specified particle size, and Defo value in the polymer, and by shifting the pH of the latex obtained into the alkaline range on completion of polymerisation.

The present invention provides a process for the production of a shaped article which process comprises (i) preparing a rubber latex, the rubber content of which has a Defo value (as herein defined) of less than 2000 and an average particle diameter of no more than 200 nm, by a procedure in which a monomer mixture of

- (a) 85 to 50 parts by weight of butadiene and/or isoprene,
- (b) 10 to 40 parts by weight of acrylonitrile and/or methacrylonitrile,
- (c) 0 to 40 parts by weight of styrene,
- (d) 0 to 10 parts by weight of acrylamide and/or methacrylamide and/or at least one N - methylol, ether, ester or urethane derivative thereof and
- (e) 0.1 to 10 parts by weight of at least one  $\alpha,\beta$  - unsaturated carboxylic acid,

is polymerised at a temperature of from 10 to 80°C in aqueous emulsion at pH below 7 in the presence of a polymerisation initiator, a molecular weight modifier and an emulsifier which consists of at least one alkylaryl-sulphonate in an amount of 0.5 to 6.0% by

50

55

60

65

70

75

80

85

90

weight, based on total monomer, and optionally at least one other surface-active substance in an amount of 0 to 5% by weight, based on total monomer, (ii) adjusting the pH of the latex to above 8 with alkali metal hydroxide, and (iii) precipitating rubber from the latex by contacting it with a coagulant.

A mould may be coated with the coagulant, and then with the latex, thereby forming a film of rubber on the surface of the mould. Alternatively, the latex may be extruded into a bath of the coagulant to form a continuous, shaped rubber article.

With these latices, smooth films of adequate thickness are obtained on the moulds by the "Koagulant" process, these films having superior strength and tear resistance after vulcanisation.

The latex is prepared by conventional emulsion copolymerisation procedures at an acid pH, normally in the range of from 2.5 to 6.

It has proved to be advantageous to add the emulsifier either continuously or in portions during polymerisation.

Alkylaryl sulphonate emulsifiers which contribute particularly to favourable coagulation behaviour of the latex processing are, alkali metal salts. The alkyl group can be linear or branched and can contain from 4 to 18 carbon atoms. The aryl group may be based on a mononuclear or polynuclear aromatic hydrocarbon. The sodium salts of dodecylbenzene sulphonic acids are mentioned as one example. In addition to one or more emulsifiers of the alkylaryl sulphonate type, it is also possible to use other emulsifiers in quantities of up to 5.0% by weight, based on total monomer. Alkali metal sulphonates and sulphates of  $C_{12}$ — $C_{18}$  hydrocarbons, and non-ionic emulsifiers known for this purpose in the art, can be used as the additional emulsifiers.

Polymerisation is carried out in the presence of the usual initiators and molecular weight modifiers at temperatures in the range of from 10 to 80°C. Organic peroxide compounds can be used as initiators in quantities of from 0.01 to 2.0% by weight, based on total monomer. Examples of suitable modifiers include aliphatic mercaptans and dithioxanthogenates preferably used in quantities of from 0.01 to 5% by weight, based on total monomer.

Butadiene, isoprene and (methacrylonitrile and, to a lesser extent, optionally styrene are used as the principal monomers. The use of excessive quantities of styrene and deficient quantities of (meth)acrylonitrile results in dipped articles having only a moderate resistance to solvents. Thus, polymer dispersions consisting solely of styrene and butadiene are unsuitable for certain applications.

The polymer dispersions contain other re-

active group-containing monomers in smaller quantities than the principal monomers referred to above. These additional monomers are essentially  $\alpha,\beta$  - unsaturated carboxylic acids and, optionally, carboxylic acid amides or reaction products of carboxylic acid amides. Examples of suitable  $\alpha,\beta$  - unsaturated carboxylic acids include acrylic acid, methacrylic acid, maleic acid, fumaric acid and itaconic acid. In addition to acrylamide and methacrylamide, it is also possible to use their N-methylol compounds, ethers, ester or urethane derivatives.

Thus, the most favourable composition for the polymers is as follows: 85 to 50 parts by weight of butadiene units, 10 to 40 parts by weight of (meth)acrylonitrile units, 0 to 20 parts by weight of styrene units, 0.1 to 10 parts by weight of  $\alpha,\beta$  - unsaturated carboxylic acid units, and 0 to 10 parts by weight of (meth)acrylamide and/or methylol derivatives thereof.

Polymerisation is stopped after the required conversion has been obtained. Polymerisation can be stopped by adding substances of the kind which are able to break off any radicals present and to destroy activator residues, for example sodium hydrogen sulphite, sodium dithionite, Rongalite (Registered Trade Mark), hydroxylamine, dialkylhydroxylamines, hydrazine or sodium dimethyl dithiocarbamate.

It is recommended to continue polymerisation up to the highest possible conversion. However, the Defo-value of the polymer should not be too high, because otherwise cracked, shrinking films are obtained during the dipping process. The upper limit has been found to be a value of 2000, particularly favourable properties being obtained with polymers having Defo-values in the range of from 500 to 2000. The Defo-value can be adjusted by suitably selecting the time at which polymerisation is stopped and the quantity and dosage of modifier.

Conventional stabilisers, preferably in dispersed form, are generally added to the latices in order to protect them against the effect of light, oxygen and ozone.

A further requirement for the production of dipped articles with optimum properties is an upper limit to the average particle size of the latex. Methods for adjusting particle size, for example by suitably selecting the type and concentration of emulsifier, are already known, cf. for example Houben-Weyl, "Methoden der organischen Chemie", Vol. XIV/1, Georg Thieme Verlag Stuttgart, 1961, pages 335 *et seq* and 375 *et seq*. Smooth films having high wet gel strengths are only obtained if the average particle diameter of the latex, as determined by the light scattering method, is less than 200 nm. On the other hand, handling properties are adversely affected by the high viscosity of the latex with

oversmall particle sizes in the commercially interesting concentration range of from 35 to 60% by weight. Accordingly, a latex satisfying processability requirements should have an average particle size of no more than 200 nm, preferably in the range of from 70 to 200 nm.

The solids concentration of 35 to 60% by weight which the latex preferably has to provide both for favourable processability and for adequate wall strengths of the dipped articles can be obtained by polymerising monomer emulsions of corresponding concentration or by increasing the concentration of a so-called thin latex by the evaporation of water, creaming or centrifuging.

Dipped articles with sufficiently thick walls and with a smooth surface can be obtained in short dipping times with the copolymer latices described above. The latices can also be extruded through nozzles into a coagulant bath, in which case it is possible to obtain endless articles (for example rubber filaments), the shape of which depends upon the shape of the nozzle.

The latex used for dipping is normally provided with additives which enable the article produced to be subsequently vulcanised (crosslinked). It is possible by adding zinc oxide alone to obtain crosslinking by virtue of the carboxyl group content of the polymer. It is, however, also possible to add vulcanising agents such as sulphur, *p* - quinone dioxime, orthotolylbiguanide, *N* - cyclohexylethyl ammonium cyclohexyl ethyl dithiocarbamate, zinc - *N* - pentamethylene dithiocarbamate, zinc mercaptobenzthiazole, tetraethylthiuram disulphide; melamine - formaldehyde condensates, phenol - formaldehyde condensates or urea - formaldehyde condensates, dimethyldiphenyl thiuram disulphide, hexamethylene tetramine or sulphenamides. Unless they are soluble in water, the vulcanising agents are generally added to the latex in the form of aqueous suspensions. Quantities in the range of from 0.01 to 10% by weight, based on the solids content of the latex, are normally used. Vulcanisation is carried out over periods of 10 to 120 minutes at temperatures of from 50 to 200°C.

In many cases, the stability of the latex can be increased by adding protective colloids. Casein, cellulose derivatives or even synthetic polymers such as styrene/maleic acid ester copolymers or polyacrylic acid can be used for this purpose. Surprisingly, it has been found that, provided the limit in regard to particle size and Defo plasticity are observed, the strength properties (tensile strength and tear resistance) and, hence, the utility value of the dipped article can be significantly increased by adjusting the pH-value of the latices polymerised in the acid range to a value above 8 with aqueous solution of alkali

metal hydroxides either before or during preparation of the mixture. According to the invention, potassium hydroxide or sodium hydroxide, for example, can be used for this purpose.

Metal salts are used as coagulants in the initial dipping solution. Divalent metal ions (calcium nitrate or calcium chloride) have proved to be particularly favourable, trivalent metal ions generally resulting in overrapid coagulation. Ethanol, isopropanol, acetone, methanol and water are generally used as solvents for the coagulants either individually or in admixture with one another.

The invention is illustrated by the following Examples in which average particle diameter values were determined by a light-scattering method using an FICA-50 scattered-light photometer and evaluation according to Wesslau, corrected according to Mie. *Makromolekulare Chemie* 69 (1963), pages 213 *et seq* and 220 *et seq*, and Defo values were determined in accordance with DIN 53 514 by precipitating the latex with methanol, squeezing off the serum, washing the latex with water and drying the latex in hot air at 100—120°C.

The percentages in the Examples are by weight.

#### EXAMPLE 1

The following were introduced into a 250 litre VA-steel autoclave equipped with a stirrer, a thermometer, an inlet pipe and a thermostat:

91 kg of demineralised water,  
0.700 kg of sodium dodecylbenzene sulphonate,

0.700 kg of the sodium salt of the condensation product of naphthalene -  $\beta$  - sulphonic acid and formaldehyde,

2.333 kg of methacrylic acid (90% pure), and

3.5 g of iron (II) sulphate.

After adjusting the pH to 4.0 with aqueous ammonia,

19.6 kg of acrylonitrile, and

0.350 kg of tertiary dodecylmercaptan were added.

The autoclave was then evacuated and filled with nitrogen, and 48.3 kg of butadiene were introduced.

After heating to 22°C,

70 g of tertiary butylhydroperoxide (80%) dissolved in 700 g of acrylonitrile, and

70 g of formaldehyde sulphonylate dissolved in 1400 g of demineralised water

were added.

Samples were taken at 1 hourly intervals. After a latex concentration of 20 g of solids per 100 ml had been reached, as determined from evaporation of the samples,

- 280 g of sodium dodecylbenzene sulphonate, and  
3.5 kg of demineralised water  
were added.  
5 The temperature was then increased to 30°C.  
At latex concentrations of 30 and 35 g of solids per 100 ml,  
10 210 g of sodium dodecylbenzene sulphonate, and  
3500 g of demineralised water  
were added.  
Polymerisation was stopped at a latex concentration of 39.2% by addition of a solution of  
15 82 g of diethylhydroxylamine (85%) in 2100 g of demineralised water.  
The latex was stabilised against ageing by adding 2100 g of a 50% dispersion of styrenised xylene with a diphenylamine.  
20 The latex was heated *in vacuo* for 6 hours at 40°C in order to remove residual monomer.  
There were obtained 160 kg of latex which had a solids content of approximately 39% by weight and which contained rubber having a Defo-value of 1650 and an average particle diameter of 120 nm. One part of the latex was adjusted to pH 8.8 with 5% dilute potassium hydroxide to provide *Latex 1*. Another part of the latex was adjusted to pH 8.9 with dilute aqueous ammonia to provide *Comparison Latex A*.  
25  
30
- EXAMPLE 2**
- 35 The following were introduced into a 40 litre VA-steel autoclave equipped with a stirrer, a thermometer, an inlet pipe and a thermostat:  
12.0 kg of demineralised water,  
40 50 g of sodium dodecylbenzene sulphonate (75%)  
50 g of sodium diisobutylphenylthale sulphonate,  
0.5 g of iron (II) sulphate, and  
45 40 g of acrylic acid.  
The pH was then adjusted to 4.2 with 10% sodium hydroxide solution, followed by the addition of  
280 g of methacrylonitrile, and  
50 7 g of *n* - dodecylmercaptan.  
The autoclave was then purged with nitrogen, followed by the addition of  
680 g of isoprene.  
The autoclave was then heated to 30°C,  
55 followed by the addition of  
100 g of *p* - menthane hydroperoxide, and  
20 g of formaldehyde sulphonylate dissolved in  
200 g of demineralised water.  
60 Immediately after the onset of the reaction, the following solutions were added at constant rate over a period of 4 hours whilst maintaining the temperature at 30°C:
- Solution 1.**  
6.120 kg of isoprene,  
2.520 kg of methacrylonitrile,  
360 g of acrylic acid and  
63 g of *n* - dodecylmercaptan.  
65
- Solution 2.**  
8.0 kg of demineralised water,  
200 g of sodium dodecylbenzene sulphonate,  
30 g of formaldehyde sulphonylate and  
50 g of sodium diisobutylphenylthale sulphonate.  
70  
75
- Samples were taken at hourly intervals. 15 minutes after addition of the solutions was completed,  
20 g of *n* - dodecylmercaptan and  
50 g of methacrylonitrile  
were added.  
80  
The autoclave was then heated to 35°C and polymerisation was continued at 35°C until a latex concentration of 32 g of solids per 100 ml was reached when the reaction was stopped by the addition of  
40 g of sodium perthiocarbonate (25%)  
and  
200 g of demineralised water.  
The latex was stabilised by adding  
240 g of a 50% dispersion of a phenolic antioxidant.  
90  
The latex was heated for 4 hours at 45°C in order to remove residual monomer. There were obtained 28 kg of latex which had a solids content of approximately 30% by weight.  
95  
A solution of 40 g of sodium alginate in 5 litres of desalted water was then added to the latex. After 2 days, a thick latex which had a solids content of approximately 50% by weight and which contained polymer having a Defo value of 1800 and an average particle diameter of 150 nm was separated from the serum and adjusted to pH 9.0 with 5% sodium hydroxide solution to provide *Latex 2*.  
100  
105
- EXAMPLE 3**
- The procedure described in Example 1 was repeated except that only 120 g of tert. - dodecylmercaptan was used as modifier and polymerisation was carried out at a temperature of 40°C. There were obtained 150 kg of latex which had a solids content of 40% and which contained rubber having a Defo value of 4000 and an average particle diameter of 100 nm. The latex was adjusted to pH 9.3 with 5% potassium hydroxide solution to provide *Comparison Latex B*.  
110  
115
- EXAMPLE 4**
- The procedure described in Example 2 was repeated except that 10 g of sodium dodecylbenzene sulphonate, and  
100 g of the sodium salt of the condensa-  
120

tion product of naphthalene -  $\beta$  - sulphonic acid and formaldehyde were introduced into the autoclave, and

- 5 100 g of sodium dodecylbenzene sulphonate and  
50 g of the sodium salt of the condensation product of naphthalene -  $\beta$  - sulphonic acid and formaldehyde were introduced in the aqueous input.

10 A thick latex which had a solids content of 46% by weight and which contained polymer having a Defo value of 2000 and an average particle diameter of 230 nm was obtained and adjusted to pH 9.2 with sodium hydroxide solution to provide *Comparison Latex C*.

#### EXAMPLE 5

20 Each of the latices A, B, C, 1 and 2 produced in Examples 1 to 4 was used in the preparation of two compositions designated Mixture 1 and Mixture 2.

25 *Mixture 1* was prepared by dispersing, in 12.2 parts by weight of 5% aqueous Vultamol (Trade Mark) solution,

- 100 parts by weight of latex (dry basis),  
2.5 parts by weight of active zinc oxide,  
1.5 parts by weight of colloidal sulphur 95,  
0.8 parts by weight of Vulkacit (Trade Mark) LDA,  
30 5.0 parts by weight of glycine (10%),  
2.0 parts by weight of Bayertitan R-FKD, and

0.2 parts by weight of coloured pigment, (for example Vulkanosol (Trade Mark)). 35

*Mixture 2* was prepared by dispersing, in 9.8 parts by weight of 5% aqueous Vultamol solution,

- 100 parts by weight of latex (dry basis), 40  
1.5 parts by weight of zinc oxide RS,  
1.5 parts by weight of colloidal sulphur 95,  
1.0 part by weight of Acrafix CN (55%),  
0.6 part by weight of Vulkacit LDA,  
0.4 part by weight of Vulkacit ZP, 45  
0.4 part by weight of Vulkacit ZM,  
2.0 part by weight of Bayertitan-R-RKD, and  
0.2 part by weight of coloured pigment. (for example Vulkanosol (Trade Mark)) 50

Each of the resulting ten compositions was allowed to stand in air for 24 hours and then used in the preparation of shaped articles according to the following procedure. 55

A porcelain glove mould preheated to 50–80°C was dipped into an aqueous 50% calcium nitrate solution. After drying in air, the mould was dipped into the composition, removed from the composition after 30 minutes, dried at 70°C and vulcanised for 65 minutes at 105°C. For each of the articles thus prepared, the tensile strength and the tear resistance were measured and the visual appearance was noted. The results are shown in the following Table. 65

Latex	Tensile strength		Tear resistance		Appearance of the article Mixture 1 and Mixture 2
	Mixture 1	Mixture 2	Mixture 1	Mixture 2	
1	210	230	30	32	uniform
2	230	250	33	35	uniform
A	183	178	22	26	uniform
B	160	115	18	15	non-uniform, cracked
C	172	165	19	17	non-uniform

#### WHAT WE CLAIM IS:—

75 1. A process for the production of a shaped article which process comprises (i) preparing a rubber latex, the rubber content of which has a Defo value (as herein defined) of less than 2000 and an average particle diameter of no more than 200 nm, by a procedure in which a monomer mixture of

- (a) 85 to 50 parts by weight of butadiene and/or isoprene,  
85 (b) 10 to 40 parts by weight of acrylonitrile and/or methacrylonitrile,  
(c) 0 to 40 parts by weight of styrene,  
(d) 0 to 10 parts by weight of acrylamide and/or methacrylamide and/or at least one N - methylol, ether, ester or urethane derivative thereof and  
90 (e) 0.1 to 10 parts by weight of at least one  $\alpha,\beta$  - unsaturated carboxylic acid, is polymerised at a temperature of from 10

to 80°C in aqueous emulsion at pH below 7 in the presence of a polymerisation initiator, a molecular weight modifier and an emulsifier which consists of at least one alkylarylsulphonate in an amount of 0.5 to 6.0% by weight, based on total monomer, and optionally at least one other surface-active substance in an amount of 0 to 5% by weight, based on total monomer, (ii) adjusting the pH of the latex above 8 with alkali metal hydroxide, and (iii) precipitating rubber from the latex by contacting it with a coagulant. 105

2. A process according to Claim 1, in which a mould is coated with the coagulant, and then with the latex thereby forming a film of rubber on the surface of the mould.

3. A process according to Claim 1, in which the latex is extruded into a bath of the coagulant to form a continuous, shaped rubber article. 110

4. A process according to any of Claims 1 to 3, in which the polymerisation is carried out at a pH of from 2.5 to 6.
- 5 5. A process according to any of Claims 1 to 4, in which the rubber has a Defo value of from 500 to 2000.
6. A process according to any of Claims 1 to 5, in which the rubber has an average particle diameter of from 70 to 200 nm.
- 10 7. A process according to any of Claims 1 to 6, in which the latex has a solids content of from 35 to 60% by weight.
- 15 8. A process according to any of Claims 1 to 7, in which the precipitated rubber is vulcanised.
9. A process according to Claim 1, substantially as herein described with reference to any of the specific Examples.
10. A shaped article, when produced by a process according to any of Claims 1 to 9. 20

ELKINGTON & FIFE,  
Chartered Patent Agents,  
High Holborn House,  
52/54 High Holborn,  
London WC1V 6SH,  
Agents for the Applicants.

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1977  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.